

SCIENCE FOR CERAMIC PRODUCTION

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DIFFUSION CREEP IN OXIDE CERAMICS AND POINT DEFECTS IN CRYSTALS

V. S. Bakunov¹ and A. V. Belyakov¹Translated from *Steklo i Keramika*, No. 10, pp. 13–18, October, 2001.

Experimental data are given on the effect of thermal, impurity, and nonstoichiometric vacancies on the diffusion creep in oxide ceramics in the range of high temperatures and low mechanical loads. It is demonstrated that impurity and nonstoichiometric vacancies have the main effect on creep in a material of technical purity grade. The experimental data are adequately described in the context of the quasichemical approach, in which the concentration of vacancies is determined by the mass effect law for the respective defect-forming reactions.

Oxide ceramics subjected to mechanical loading in the range of relatively low temperatures (less than 0.5–0.7 of the melting point) exhibit brittle behavior; a certain degree of plasticity is manifested only on further heating [1]. The reason for the difference of these materials from metals and alloys consists in the ionic-covalent chemical bonds in the respective compounds. A higher value and greater orientation of the bonds between the anions and the cations determine their low mobility and thus determine the high rigidity of the crystalline lattice. In the general case, two and more types of ions, which differ in their radius, the value of the charge, and the sign, make up complex elementary cells of substantial volume, which consist of several sublattices. This results in a complex structure of the defects responsible for plasticity (dislocations, boundaries, etc.) and their gliding surfaces. This is the qualitatively reason for the brittle behavior of ceramics under mechanical loading, as well as the fact that the main mechanism of creep² in such materials at high temperatures is the diffusion-viscous flow, according to Nabarro–Herring–Lifshits [2]. Another specific feature of ceramic materials consists in their complex structure. Ceramics usually are polycrystalline solid bodies consisting of several phases, including the vitreous phase and pores, and have a multilevel structure of the fractal type [3].

The diffusion creep is observed due to the emergence of local diffusion flows between individual interface segments

of heterogeneous materials, when a mechanical load is applied (i.e., in a nonhydrostatic stress field). To be specific, we will hereafter assume that diffusion follows the vacancy mechanism, and that Schottky disordering in most cases is preferable for oxide ceramics. Then the local oversaturation of vacancies related to nonuniform distribution of normal stresses σ_n can be written as follows [4, 5]:

$$\Delta\xi \approx \xi_0; \quad \frac{\Delta\mu}{kT} = \frac{\xi_0\Omega\sigma_n}{kT},$$

where ξ_0 is the equilibrium concentration of vacancies at temperature T ; $\Delta\mu = \Omega\sigma_n$ is the alteration of the chemical potential caused by application of a mechanical load σ_n ; k is Boltzmann's constant; Ω is the atomic volume.

The self-diffusion coefficient D is related to the vacancy diffusion coefficient D_v :

$$D = N_v D_v,$$

where N_v is the vacancy concentration.

The sources and sinks of vacancies in the considered model are the external and internal surfaces (pores) of the body, the boundaries of crystals or blocks, and dislocations, their power abruptly decreasing in the above sequence. The most energy-consuming process of vacancy migration is their diffusion inside the crystal volume before reaching the interface, whose permeability is significantly higher. A consecutive consideration of diffusion creep was carried out in [6], which took into account the contributions of the volume diffusion D_{vol} and boundary diffusion D_b coefficients. The later prevails in materials with a developed boundary grid,

¹ Joint Institute of High Temperatures of the Russian Academy of Sciences, Moscow, Russia; D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

² Creep is the capacity of a material for slow plastic deformation under the effect of a relatively low constant mechanical load.

when the pathway of a vacancy inside the volume is not long, whereas $D_{\text{vol}} < D_b$.

The temperature dependence of the diffusion coefficient is described by the Arrhenius equation:

$$D = D_0 \exp\left(-\frac{Q}{kT}\right),$$

where Q is the activation energy, and the pre-exponential member D_0 includes the activation entropy.

The value Q comprises the sum of the energy of vacancy formation U and the energy ω of migration of vacancies [7]:

$$Q = U + \omega.$$

According to the above, there is a distinction between the energy of vacancy migration inside a volume ω_{vol} and along the boundaries ω_b of the crystals (where $\omega_{\text{vol}} > \omega_b$), as well as along other interface surfaces and dislocations.

The removal of any ion from the lattice in ionic-covalent crystals leads to the formation of an oppositely charged vacancy, whose charge is a multiple of the electron charge. The following types of point defects are distinguished depending on their origin: inherent thermally activated defects, impurity, and nonstoichiometric defects. The formation of defects is limited by several conditions related to the crystal structure. Thus, the constancy of the lattice points in various sublattices is maintained. To preserve the general electric neutrality and the absence of electric current in a crystal, a certain ratio should be preserved between the concentration of cation and anion vacancies and their flows. Thus, one can speak of self-coordination of the diffusion of ions of different signs (their vacancies) in ceramics.

The formation of the specified types of vacancies can be described by quasichemical reactions of disordering in accordance with the chemical thermodynamics and kinetics laws [8]. Usually the accepted model correlates with the diluted solution approximation, when the interaction between the vacancies can be neglected due to their low concentration. This model is effective up to an atomic content about 1%. By the law of mass effect, it is possible to obtain equations relating the concentrations of defects for every type of disordering, whereas the activation energy of the described reactions characterizes the energy of defect formation. The reactions of formation of inherent defects consume substantial energy, and the concentration of such vacancies is usually very low. The impurity and nonstoichiometric vacancies are easily formed, and their concentration correlates with the concentration of heterovalent impurities or with the degree of deviation from stoichiometry [9].

In the case of mass transfer in a mechanical stress field, the aforesaid provides a basis for dividing ceramic materials as objects of study into three ultimate types: pure materials with a stoichiometric composition, stoichiometric materials with impurities, and pure materials with deviations from stoichiometry. It should be noted that in practice we encoun-

ter materials that have a combination of the specified defects and, possibly, even the simultaneous presence of all defects.

The value of the effective diffusion coefficient is determined by the concentration of defects, as well as their mobility, which depends on the diffusion pathway (in the volume or along the boundaries) and exponentially grows with increasing temperature. The concentration of inherent defects is related to thermal fluctuations, which contributes to the process activation energy. The presence of a significant fixed amount of heterovalent impurities (below the limit of their solubility in the crystal) determines a constant number of vacancies in a rather wide temperature interval and is not related to thermal fluctuations. An excess or a deficit of oxygen in the cases of deviations from stoichiometry has the same effect as the existence of impurities in its sublattice with the formation of the respective vacancies.

It can be supposed that within a relatively narrow temperature interval in which the creep is reliably identified in practice, for each particular material a unique constant diffusion mechanism of deformation will presumably be registered, which corresponds to the type of the limiting defect and which determines the specific value of the process activation energy. However, inflections in the temperature dependence curves are possible as well, corresponding to modifications in the material structure.

It is noteworthy that impurities are present in most types of currently used ceramics in perceptible quantities, and their range is rather wide, depending on the type of material used and on the degree of refinement, including metals with variable valence. It appears that the role of impurity and nonstoichiometric defects in creep is crucial for ceramic materials, since a solution of thermally activated vacancies has a very high degree of dilution even near the melting temperatures. It should be stressed that impurity and nonstoichiometric vacancies only facilitate the self-diffusion of the inherent ions of the crystal; however, their contribution to mass transfer is insignificant due to the low concentration of impurities and small deviations from stoichiometry, compared to the number of lattice points.

The present study is dedicated to the consideration of the effect of point defects on high-temperature creep in ceramics from the point of view of the experimenter. The experiments were conducted at temperatures up to 1800–1900°C within the load interval 0.5–2.5 MPa in inert gas medium (helium) [10]. In the course of experiments, the deformation kinetics ε was registered before and after a slight temperature jump (50°C) under a constant mechanical load, and also before and after an increase in the load (approximately 2 times) under a constant temperature; a constant degree of deformation was reached at each stage. The registered rate of pure bending deformation $d\varepsilon/dt$ varied within the limits $10^{-5} - 10^{-1} \text{ h}^{-1}$.

The experimental data were obtained on samples of polycrystalline densely sintered ceramics having zero open porosity and total porosity up to 1–3%, made of materials of “technical purity” grade with overall content of impurities up

to 0.3 wt.%. Such selection makes it possible to exclude the effect of pore inclusions and a low-melting vitreous phase on the measurement results.

The samples were made by semidry molding of finely disperse powders (particle size below 1–3 μm) and subsequent sintering. Considering the low mobility of extended structural defects (dislocations, boundaries) in ceramics, an assumption can be made that the role of the point defects in this case will be prevailing. Indeed, the experimental data [11, 12] satisfy all specifics of the diffusion creep [13]: rectilinear deformation kinetics, direct proportionality of the creep rate to the applied stress, the inverse proportionality of the creep rate to the square or cube of the crystal size, and correlation of the creep activation energy with the activation energy of point defect diffusion. The occasional deviations from the specified regularities are due to structural modifications.

Figure 1 shows the temperature dependence of the creep rate in corundum ceramics without additives and with magnesium oxide and titanium dioxide additives. As can be seen, the experimental dependences $\log (d\varepsilon/dt) - f(1/T)$ for these samples virtually coincide. The registered divergence of the dependences in the selected coordinates is insignificant and can be totally accounted for by the instrumental error or by the variations in the structural characteristics of the samples (for instance, samples with TiO_2 additive consisted of larger crystals). All this corroborates the assumptions ensuing from the quasichemical approach [8], implying that the energy of vacancy formation for relatively low concentrations of impurity centers correlates with the inherent thermal disordering. Consequently, the creep activation energy in general does not vary, although a certain change in the vacancy concentration depending on the type of additive can, accordingly, modify the process rate. The relatively low activation energy (for the results shown in Fig. 1 it is 400–500 kJ/mole) points to the contribution of the boundary diffusion in this case.

Such conclusions are corroborated by the results in Fig. 2, which shows the temperature dependence of the creep rate in corundum ceramics made of extra-pure material, compared to material of “technical purity” grade. After processing, the overall weight content of impurities in the extra-pure samples is equal to $10^{-3}\%$, i.e., lower by approximately two orders of magnitude than in the technical grade samples. The use of extra-pure material decreases by an order of magnitude the deformation rate under the given temperature and given load, whereas the process activation energy does not change. The decreased concentration of impurity centers probably determines the decrease in the creep rate, whereas the constant activation energy (see Fig. 1) correlates with the decisive influence of internal disordering.

The effect of modification in the phase composition on creep in polycrystalline materials can be considered using the example of ceramics in the system $\text{MgO} - \text{MgAl}_2\text{O}_4$. During the synthesis and sintering of ceramics in repeated firing, the spinel formation reaction proceeds to the end [14].

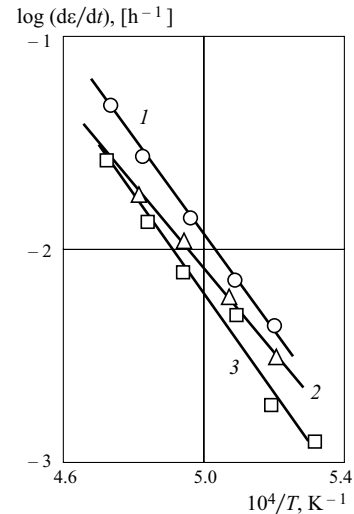


Fig. 1. Creep in corundum ceramics under pressure 1.3 MPa without additives (1) and with additives 0.3 wt.% MgO (2) and 1 wt.% TiO_2 (3).

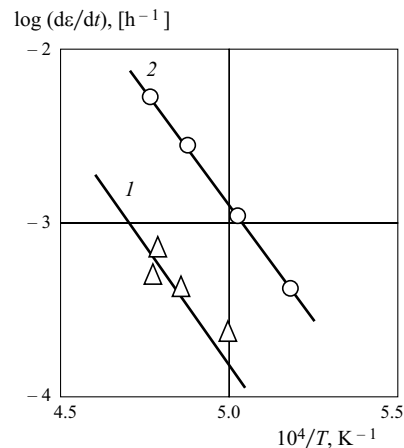


Fig. 2. Creep in corundum ceramics made of extra-pure material (1) and technical grade material (2) under pressure 2.5 MPa; crystal size 20–30 μm .

Judging from the phase diagram [15], the compositions adjacent to pure components contain single-phase areas of solid solutions of aluminum oxide in magnesium oxide and magnesium oxide in spinel, the homogeneity area of the latter solution being smaller.

The structure of the samples of intermediate compositions (15–65 wt.% aluminum oxide) is a fine-crystalline mixture of periclase crystals and aluminomagnesium spinel of the eutectic type. The emergence of a rather great amount of impurity vacancies during the formation of solid solutions in the compositions adjacent to pure components decreases the effective viscosity (Fig. 3). This is related to the effect of a large quantity of impurity defects. For the solid solution of periclase in spinel, the decrease in viscosity is less perceptible, which agrees with the more narrow homogeneity area in

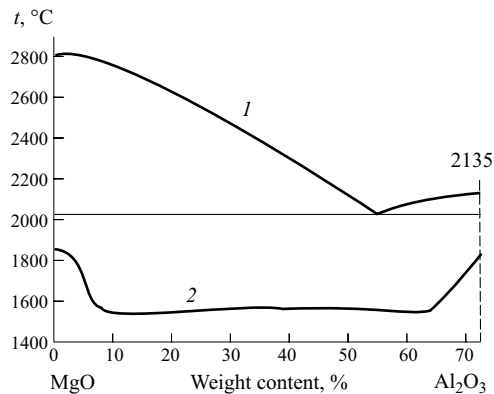


Fig. 3. Dependence of liquidus temperature (1) and apparent viscosity (2) on the composition of samples in system $\text{MgO} - \text{MgAl}_2\text{O}_4$ ($\eta = \frac{\sigma}{d\varepsilon/dt} = 3 \times 10^{13} \text{ Pa} \cdot \text{sec}$).

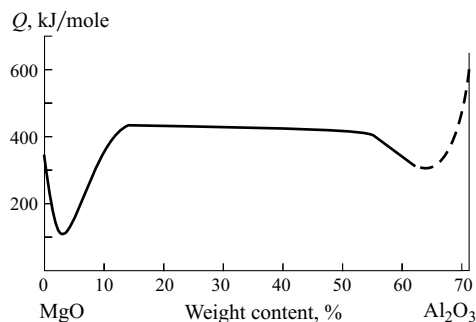


Fig. 4. Creep activation energy Q of ceramic samples in system $\text{MgO} - \text{MgAl}_2\text{O}_4$.

this case. After that the vacancy solution becomes saturated (i.e., transforms from a diluted solution to a concentrated one), and a second phase (periclase or spinel) is formed in it. Therefore, the viscosity of the intermediate compositions, i.e., the viscosity of the relatively low-melting fine-crystalline eutectic mixture, is virtually constant, which agrees with the similar structure of the samples in spite of the fact that the liquidus temperature in this range changes significantly.

The creep activation energy (Fig. 4) changes nonmonotonically depending on the composition: it has minima in the ranges adjacent to pure components, and in the middle part this energy is constant. This variation correlates with the considered quasichemical approach: the minimum activation energy presumably correlates with the highest solubility of the second component, and a further increase correlates with the second phase formation.

The effect of nonstoichiometric oxygen vacancies on creep was investigated on ceramics based on cerium dioxide. It is known [16] that cerium dioxide in a reducing medium loses oxygen and passes via a continuous sequence of solid solutions to oxides of lower degrees of oxidation with the

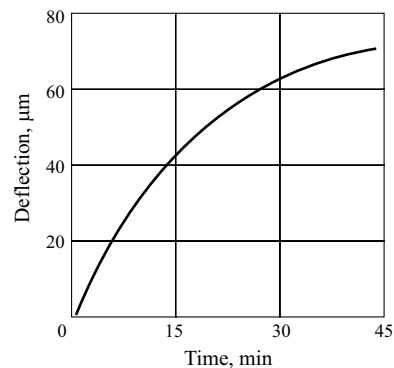
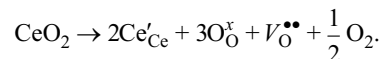
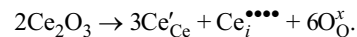


Fig. 5. Creep curve in cerium dioxide ceramics in a reducing medium at temperature 1350°C and pressure 0.7 MPa .

emergence of oxygen vacancies. The defect formation reaction can be written in the following way:



The initial ceramic samples had a virtually stoichiometric composition after being fired in a reducing medium. They were tested in an inert atmosphere (helium) in a furnace with a tungsten heater, in which a low partial pressure of oxygen was set corresponding to the equilibrium pressure on top of tungsten for the particular temperature. The creep deformation in time (Fig. 5) had the form of smoothly attenuating curves, due to a continuous increase in the quantity of nonstoichiometric vacancies. Their formation was retarded when the concentration approached the equilibrium value for the specified partial oxygen pressure. This can be attributed to a possible defect-forming reaction, when part of cerium cations migrate to the interstices, which decreases the number of oxygen vacancies:



The experiments designed according to a special method made it possible to estimate the temperature dependence of the creep rate for different degrees of reduction (Fig. 6) and calculate the creep activation energy (Fig. 7). The testing of the samples with stoichiometric compositions was conducted in air. It can be seen that under low degrees of reduction, an increase in the creep rate is observed for the given temperature and load; however, the activation energy varies little. The increment of the creep rate abruptly decreases at $x = 1.950 - 1.925$, and the activation energy as well significantly drops within this interval. On further reduction up to $x = 1.875$, both the creep rate and the activation energy virtually do not change.

Thus, the constant activation energy and increasing creep rate are observed up to the composition $\text{CeO}_{1.95}$, which corresponds to 2.5% nonstoichiometric vacancies. It can be assumed that roughly this amount of vacancies is the limiting quantity, up to which the behavior of the samples is deter-

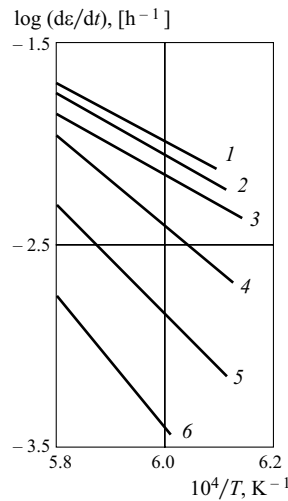


Fig. 6. Creep (pressure 1.4 MPa) of cerium dioxide ceramics. The value x in CeO_x is: 1) 1.875; 2) 1.900; 3) 1.925; 4) 1.950; 5) 1.975; 6) 2.000.

mined by their internal disordering. In the further evolution of the process, nonstoichiometric vacancies prevail (in this case, the anion ones), whereas the activation energy decreases. The increase in the creep rate can be also related to the fact that these experiments demonstrate the role of vacancies at the moment of their origin. It is known that the mobility of atoms (and defects) is significantly intensified during the reactions. In particular, the plasticity of materials increases during phase transformations, what is known as the transformation plasticity [4].

This point of view is substantiated by the results of studying corundum ceramics with titanium dioxide additive (Fig. 8). Titanium dioxide in a reducing atmosphere loses oxygen and passes to the lower degrees of oxidation [16]. The data in Fig. 8 indicate that samples that have been oxidized in firing lose oxygen in the reducing medium of the experimental furnace with the formation of vacancies, which significantly enhances the creep rate, compared to the creep rate of reduced samples. It can be assumed as well that due to the low concentration of the impurity cation vacancies available in the material and the newly formed nonstoichiometric anion vacancies, they do not interact: vacancies in a diluted solution are "not aware" of each other, i.e., the field forces of two neighboring vacancies even of the opposite signs do not overlap.

One should note the phenomena related to the coloring of samples after testing. In accordance with the defect formation reactions [8], in the presence of impurities (or additives) with a constant degree of oxidation (Al_2O_3 to MgO and MgO to MgAl_2O_4), electron defects and, accordingly, color centers are not formed in the ionic crystals. In contrast, in the case of a deviation from stoichiometry, when the oxygen partial pressure decreases compared to the equilibrium value, anion vacancies and free electrons are formed, which join and produce F -centers. If fact, no variation in color was observed after testing in the first case, whereas in all cases of the alteration of the degree of cation oxidation, significant darkening of the sample was registered, especially in corun-

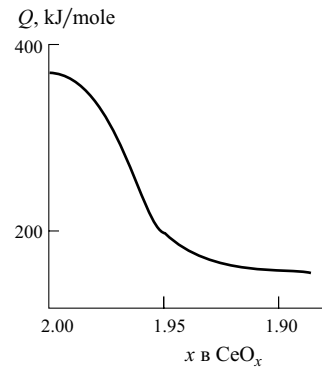


Fig. 7. Creep activation energy Q of cerium dioxide ceramics.

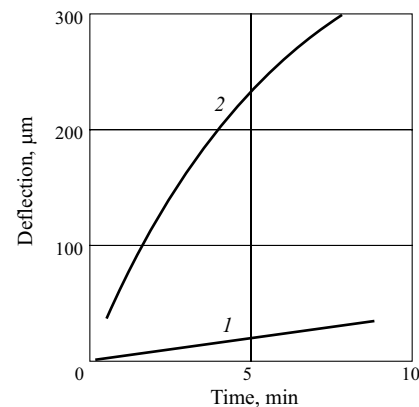


Fig. 8. Creep curve at temperature 1650°C and pressure 1.3 MPa in corundum ceramics with 1 wt.% TiO_2 additive in a reducing medium after heat treatment in reducing (1) and oxidizing (2) atmosphere.

dum ceramics, to which only 1 wt.% titanium dioxide was introduced.

Judging from the available data, it can be inferred that high-purity ceramics of stoichiometric composition is the most resistant to creep, due to its very low concentration of thermally activated vacancies. Impurities even in low quantities (fraction of a percent) abruptly enhance the creep rate due to a substantial increase in the concentration of vacancies (by one order of magnitude). The process activation energy in this case varies little, since the internal disordering reactions act as the limiting factor. In materials of technical purity grade, introduction of additives in quantities corresponding to a diluted vacancy solution (atomic content up to 1 – 2%) has virtually no effect on the creep process. In the range of concentrated solid solutions, i.e., when vacancies interact, the deformation rate remains virtually constant, the process activation energy decreases, and the concentration of vacancies is determined by the reactions of impurity center formation. In the range of formation of the second phase crystals, the activation energy keeps growing up to a constant level, while the deformation rate virtually does not change.

To conclude, we would like to observe that the high-temperature deformation properties of ceramic materials can be controlled by introducing point defects via doping with the respective impurities or by deviation from stoichiometry. This is a promising way for controlling high-temperature deformation in densely sintered ceramics of special destination, ceramic matrix in ceramic-metal materials, the skeleton of porous polycrystalline ceramics, etc.

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